

UDC 666.293.521.4.001.8

ONE-COAT FLUORINE-FREE ENAMELS WITH A DECREASED COBALT OXIDE CONTENT

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Translated from *Steklo i Keramika*, No. 5, pp. 30 – 31, May, 2001.

The effect of variable-valence oxides on the adhesion strength and elasticity of one-coat fluorine-free coatings is studied. The possibility of lowering the cobalt oxide content in the enamel composition, at the expense of introducing variable-valence oxides (NiO, CuO, and MnO₂) in the optimum ratio, without deteriorating the technological and service properties of glass enamel coatings, is established.

Owing to the scarce supply and high cost of cobalt oxide material, which is traditionally used to ensure the strength of adhesion in one-coat enamels, we investigated the possibility of using manganese, iron, nickel, and copper oxides as adhesion activators, as well as reducing the cobalt oxide content in the composition of enamels. The above-listed oxides act as fluxes in silicate melts, improve the chemical resistance of glasses, and intensify the effect of adhesive oxides [1, 2]. The studies in [3 – 5] considered the effect of variable-valence oxides on the adhesion of one-coat enamels; however, in most cases, these were fluorine-bearing enamels.

The effect of variable-valence oxides on the adhesion strength in a one-coat fluorine-free coating in the absence of cobalt oxide was investigated based on the initial glass of the following composition (here and elsewhere in wt.%): 63.0 SiO₂, 3.2 TiO₂, 1.9 Al₂O₃, 11.0 B₂O₃, 3.9 RO, 17.0 R₂O. Cobalt oxide was introduced in the enamel glass composition (above 100%) in the amount of 0.25 – 1.00%, whereas the content of nickel, copper, iron, and manganese oxides amounted to 1 – 4%.

All enamels were melted in a silite electrical furnace at a temperature of 1350°C in porcelain crucibles of 200-ml capacity. The capacity for coating formation was tested in a gradient furnace. The experiment determined the starting temperature of coating fusion, the spreadability of enamel glasses (OST 26-01-198–79), and their chemical resistance to 10% HCl solution and 1 N NaOH solution, using the granular method based on the weight losses in heating on a water bath (98°C) for 1 h.

The main parameters of the enamel glasses are given in Table 1. It can be seen that on adding 1% oxides to the initial composition, the spreadability of all enamel glasses improves. The oxides can be arranged in the following series

based on their effect on spreadability: Co₂O₃, NiO, Fe₂O₃, CuO, and MnO₂.

When added in the amount of 4%, nickel, iron, and manganese oxide improve the spreadability of enamel glass more effectively than copper oxide does. The introduction of copper and manganese oxides significantly improves acid resistance (the weight loss decreases by 50 – 60%), and the introduction of nickel and iron oxides decreases acid resistance. A positive effect of copper oxide on alkali resistance (the weight loss decreasing by 20%) was registered as well.

The adhesion of enamel to steel was determined using a device developed at the Novocherkassk State Technical University, using the method of gradient deformation of samples coated by obtained glass enamels.

The samples made of steel 08 kp had a size of 59 × 59 × 1 mm. The ultimate extraction depth was 7 mm. The state of the coating was checked after each millimeter of extraction. The steel samples were prepared by thermal degreasing at 820°C with subsequent pickling in 20% hydrochloric acid. The slip method was used in deposition of the coating, and then the sample was fired for 3 min at the temperature needed to get a high-quality lustrous coating.

Figure 1 shows the effect of cobalt, nickel, and copper oxides on the adhesion index. Nickel oxide in an amount above 1% has a greater effect on the strength of adhesion of enamel to the substrate than copper oxide, which can ensure an adhesion index above 80% only when its content exceeds 4%.

Copper and nickel oxides, when introduced in the amount of 3 – 4%, affect the strength of adhesion in the enamel – metal system, which is equivalent to the effect to 0.5 – 1.0% cobalt oxide: the adhesion index is equal to 80 – 98% and the metal deformation is 2 mm.

The visual appraisal of the coating destruction identified the emergence of single cracks at the initial stage of deforma-

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tion (1–2 mm) and breaking off of the enamel coating under a greater degree of deformation (3–4 mm). The color of metal in the break-off site makes it possible to characterize not only the effect of oxides on the adhesion strength but their effect on the coating elasticity as well. The introduction of 3–4% nickel oxide into the enamel composition has a more favorable effect on the elasticity of the coating than the introduction of the same quantity of copper oxide, since the flaking process in the latter case is more intense, and only a thin dark-red layer of copper is observed in the damaged site in the spot of break-off. It is inadvisable to use iron and manganese oxides as independent adhesive oxides, since they do not ensure the required strength of adhesion. However, their introduction into the glass composition improves its spreadability and lowers the starting temperature of the coating fusion, which can contribute to increasing adhesion on the enamel–metal interface.

Based on the studied regularities, a one-coat enamel 21P was synthesized, which contains 3% NiO and 4% MnO₂ and has an adhesion index of 100% with the deformation of metal equal to 1 mm. However, with the deformation equal to 2 mm, the coating becomes destroyed, which means that the elasticity of the coating is insignificant (Fig. 2).

To increase the elasticity of the coating (to preserve its integrity under a deformation of metal equal to 2 mm or more), it is necessary to introduce at least 0.5% Co₂O₃ (composition 2P). However, on adding nickel, copper, and manga-

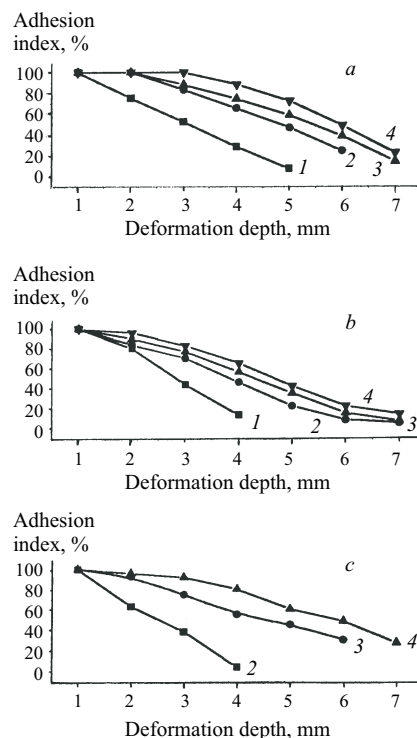


Fig. 1. Dependence of the adhesion index of the coating on the depth of metal deformation. Weight content of Co₂O₃ in coating (a): 1) 0.25%, 2) 0.50%, 3) 0.75%, 4) 1.00%; content of NiO in coating (b): 1) 1.0%, 2) 2.0%, 3) 3.0%, 4) 4.0%; content of CuO in coating (c): 2) 2.0%, 3) 3.0%, 4) 4.0%.

TABLE 1

Compo- sition	Mass content of adhesive oxides, %					Fusion start temperature, °C	Spread- ability at 860°C, mm	Chemical resistance (weight loss), %	
	Co ₂ O ₃	NiO	CuO	Fe ₂ O ₃	MnO ₂			in 10% HCl	in 1 N NaOH
P	—	—	—	—	—	820	25.9	0.39	2.15
1P	0.25	—	—	—	—	820	24.5	0.45	2.13
2P	0.50	—	—	—	—	820	24.6	0.48	2.15
3P	0.75	—	—	—	—	810	26.4	0.50	2.23
4P	1.00	—	—	—	—	810	30.1	0.50	2.34
5P	—	1.0	—	—	—	820	29.6	0.42	2.11
6P	—	2.0	—	—	—	820	29.7	0.42	2.05
7P	—	3.0	—	—	—	815	29.9	0.44	1.99
8P	—	4.0	—	—	—	800	32.2	0.98	1.68
9P	—	—	1.0	—	—	820	27.4	0.16	1.65
10P	—	—	2.0	—	—	820	27.5	0.16	1.67
11P	—	—	3.0	—	—	815	28.6	0.17	1.73
12P	—	—	4.0	—	—	810	30.3	0.17	1.79
13P	—	—	—	1.0	—	810	28.8	0.76	2.11
14P	—	—	—	2.0	—	800	29.7	0.82	1.89
15P	—	—	—	3.0	—	800	31.4	1.07	1.81
16P	—	—	—	4.0	—	790	32.1	1.92	1.65
17P	—	—	—	—	1.0	800	27.0	0.18	1.87
18P	—	—	—	—	2.0	800	28.2	0.19	1.87
19P	—	—	—	—	3.0	790	29.9	0.18	1.88
20P	—	—	—	—	4.0	790	32.1	0.36	1.82
21P	—	3.0	—	—	4.0	800	33.2	0.32	1.84
23P	0.25	1.5	1.0	—	3.0	810	38.8	0.24	1.64
25P	0.25	1.5	1.0	1.0	3.0	810	35.4	0.60	1.45

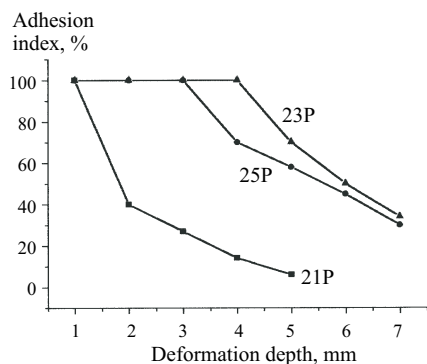


Fig. 2. Dependence of the adhesion index of developed enamels on the depth of metal deformation.

nese oxides in the ratio of 1.5 : 1 : 3, the cobalt oxide content can be reduced to 0.25% (compositions 23P and 25P). These coatings have satisfactory adhesion (adhesion index 95 – 100%), increased elasticity (with the metal deformation equal to 3 – 4 mm, the coating does not flake), a high mirror reflection coefficient (60 – 62%), good technological parameters (spreadability 37 – 39 mm, firing interval 105°C) and good service properties (impact strength 5 J, heat resistance 300°C).

Thus, the possibility of reducing the cobalt oxide content in the composition of one-coat fluorine-free enamel to 0.25% at the expense of introducing nickel, copper, and manganese oxides in the optimum ratio, without deteriorating the technological and service properties of enamel coatings, was established.

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